

Interaction Between Polyacrylonitrile and Alkalis

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Received 27 September 2004; accepted 3 May 2005

DOI 10.1002/app.23725

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Interactions between highly isotactic acrylonitrile homopolymers and alkalis in dimethyl sulfoxide solvent were examined. Coloration occurred as soon as polyacrylonitrile was added to a dimethyl sulfoxide/alkali mixture. The effects of alkali on highly isotactic polyacrylonitrile were greater than those on ordinary polyacrylonitrile. The intrinsic viscosity of polyacrylonitrile decreased quickly with the addition of sodium ethoxide and sodium hydroxide, and the effect of sodium ethoxide was more prominent than that of sodium hydroxide. As the concentration of sodium ethoxide and sodium hydroxide went beyond 0.01 mol/L, the intrinsic viscosity showed a trend of increasing. Within the first half-hour, there was a great drop in the

intrinsic viscosity of highly isotactic polyacrylonitrile, and then the intrinsic viscosity appeared to increase. The intrinsic viscosity of highly isotactic polyacrylonitrile increased continuously with the addition of diethylamine along with time. The effects of alkalis on the tacticity of the polymers followed the order of the alkali strength. Diethylamine was more effective for moderating the stabilization exotherm of polyacrylonitrile than sodium ethoxide and sodium hydroxide. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 272–275, 2006

Key words: additives; viscosity

INTRODUCTION

Acrylonitrile polymer based precursors are emerging as some of the best materials for making carbon fibers, and the properties of the final carbon fibers are determined by the nature of the precursor fibers. It is important to select a highly stereoregular acrylonitrile polymer for high-tenacity acrylic fibers.¹ The stabilization process of polyacrylonitrile precursors is essential for converting the fibers into an infusible form in air via heating between 200 and 300°C. Many reagents have been reported in the literature^{2–6} as pretreatments for reducing the viscosity of acrylonitrile polymers and moderating the stabilization exotherm, and high-performance carbon fibers have been obtained. The effects of inorganic salts and acids on the viscosity of acrylonitrile polymers have been observed and reported in the literature.^{7,8} In one case, the addition of LiCl to the spinning dope reduced the viscosity of the dope and moderated the stabilization exotherm of the precursors.⁹ To our knowledge, there are only a few reports on the pretreatment of ordinary acrylonitrile polymers, but there is almost no report on highly isotactic acrylonitrile polymer. Little work has been

done on alkali as an additive. With this view, studies in contrast were undertaken on the interaction between alkali and highly isotactic polyacrylonitrile (MAP) in the solvent dimethyl sulfoxide (DMSO). In this study, a matrix–anion polymerization technique was used to synthesize the acrylonitrile homopolymer. The intrinsic viscosity ($[\eta]$) of polyacrylonitrile was controlled and determined by the Ubbelohde viscometer. The interactions between alkalis of different strengths and MAP and ordinary polyacrylonitrile (WSP) were studied.

EXPERIMENTAL

Homopolymers

MAP was prepared by matrix–anion polymerization technology. The details of the polymerization technology are given in the literature.^{10,11} For comparison, WSP, synthesized by water–solvent (DMSO) suspension polymerization,^{12,13} was also used. The characteristics of the polymers are given in Table I. Sodium ethoxide, sodium hydroxide, and diethylamine were supplied as extrapure-grade by Shanghai Chemical Resin Industry (Shanghai, China).

Characterization

$[\eta]$ of these homopolymers in dimethylformamide solutions was determined with an Ubbelohde viscome-

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Contract grant sponsor: Department of Science and Technology of Shandong Province and Yantai Normal University.

TABLE I
Important Parameters of the Samples

Sample code	Polymerization technology	$[\eta]$	Triad tacticity		
			(<i>mm</i>)	(<i>mr</i>)	(<i>rr</i>)
MAP	Matrix-anion	1.74	0.613	0.285	0.102
WSP	Water-DMSO suspension	2.76	0.291	0.502	0.207

ter kept vertically in a thermostatic bath at the required temperature of 25°C ($\pm 0.05^\circ\text{C}$).

The polymers were poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C *in vacuo* before NMR and differential scanning calorimetry (DSC) characterization.

The triad tacticities [(*mm*), (*mr*), and (*rr*), where *m* and *r* are meso and racemo dyad sequences, respectively] of polyacrylonitrile were determined on the basis of Schaefer's assignment¹⁴ from the ratio of the intensities for the three nitrile carbon peaks in the ¹³C NMR spectra. ¹³C NMR spectra were recorded on a Bruker (Germany) DPX300 spectrometer in a 2.5 wt % solution in deuterated DMSO at 80°C under the following operating conditions: complete decoupling mode, a pulse delay time of 1.745 s, an acquisition time of 0.655 s, a pulse width of 5.5 μs (45° pulse), and an accumulation of more than 3000 times.

DSC spectra of polyacrylonitrile were determined on a PerkinElmer Delta thermal analyzer. DSC studies were performed at a heating rate of 5°C/min in oxygen with a sample of 2.5 mg; this was much like the conditions of stabilization of the polyacrylonitrile precursors. The values of the exotherm of polyacrylonitrile during the stabilization process were calculated from DSC spectra.

RESULTS AND DISCUSSION

Effect of the alkali concentration on $[\eta]$ of polyacrylonitrile

For our initial experiment, two strong bases, sodium ethoxide and sodium hydroxide, and a weak base, diethylamine, were used. Alkali was first added to the solvent DMSO, and then polyacrylonitrile was dissolved in a DMSO-alkali mixture to give a solution. The solution was stirred for half an hour at 25°C until a transparent and viscous complex was obtained. As soon as polyacrylonitrile was added to the mixture, the polymer dissolved, and coloration occurred simultaneously. The solution containing diethylamine did not become as dark as the solution containing sodium ethoxide and sodium hydroxide.

The effect of alkali on $[\eta]$ of polyacrylonitrile was studied by the variation of the concentration of alkali from 0 to 0.035 mol/L. Figures 1 and 2 illustrate $[\eta]$ of

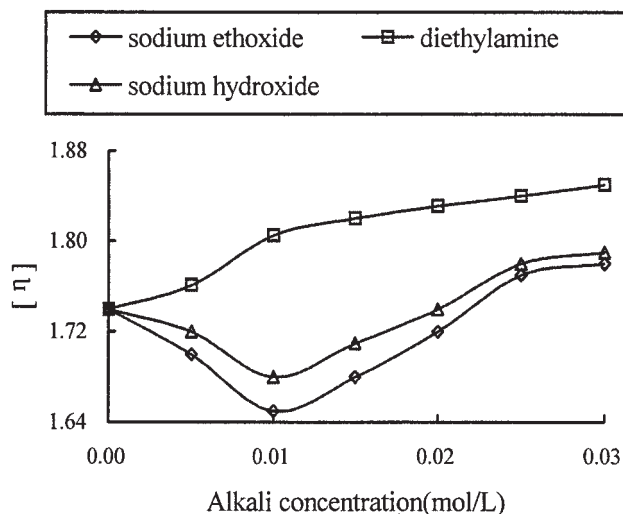


Figure 1 Effect of alkali on $[\eta]$ of MAP polymers.

MAP and WSP as a function of the alkali concentration, respectively. There was a great drop in $[\eta]$ of the polymer containing sodium ethoxide and sodium hydroxide, and then $[\eta]$ showed a trend of increasing when the concentration of alkali was greater than 0.01 mol/L. $[\eta]$ of the polymer containing diethylamine did not drop but tended to increase. Changes in $[\eta]$ of WSP were less prominent than those of MAP. That is, the effects of alkali on MAP were more greater than those on WSP.

Alkalis were disassociated into ions by solvation effects when alkalis were put in DMSO.^{15,16} Intermolecular interaction was reduced by ions. Disentanglement and slippage of entanglement crosslinking began to occur. The introduction of alkali produced a decrease in $[\eta]$ of the polymer. As the alkali concentration went beyond 0.01 mol/L, the high molecular

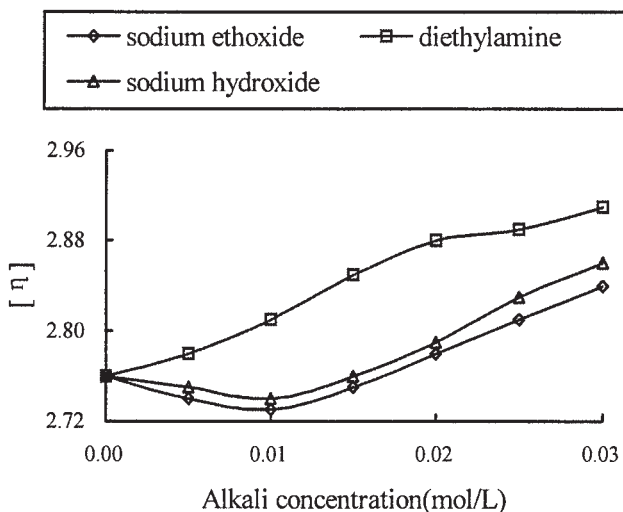


Figure 2 Effect of alkali on $[\eta]$ of WSP polymers.

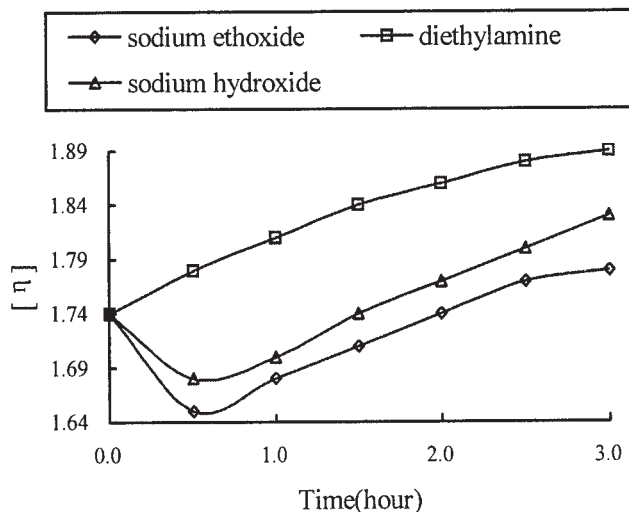


Figure 3 Effect of time on $[\eta]$ of MAP polymers.

flow became more and more difficult; $[\eta]$ of the polymers increased slowly.

Effect of time on $[\eta]$ of polyacrylonitrile

The influence of time on $[\eta]$ of MAP was studied by the concentration of alkali being kept at 0.01 mol/L. Figure 3 shows a plot of $[\eta]$ against time. Within the first half-hour, there was a great drop in $[\eta]$ of MAP containing sodium ethoxide and sodium hydroxide, and then $[\eta]$ appeared to increase. Batty and Guthrie¹⁷ indicated that the rapid $[\eta]$ drop was due to random chain scission and that the polymer chains coiled tightly. Bashir et al.¹⁸ also reported an increase in $[\eta]$ with sodium hydroxide after an initial drop. The $[\eta]$ increase was probably due to a limited amount of crosslinking. Gelation was observed, and a dark red-black gel was formed 5 h later.

$[\eta]$ of the polymer containing diethylamine did not drop but increased along with time. After a few hours, changes in $[\eta]$ became less prominent, and this was in agreement with the literature.¹⁹

Correlation between alkalis and tacticity changes of polyacrylonitrile

Because alkalis play an important role in the factors that affect the tacticity of polymers, the effect of alkalis on the tacticity of polyacrylonitrile is discussed. The tacticity of the homopolymers was determined by triad tacticity through NMR measurements. A comparison of the nitrile bands of alkali-treated MAP and untreated MAP in Figure 4 shows that the addition of a base caused a marked change in the tacticity. There was a remarkable drop in the isotactic triad levels, and there was a simultaneous increase in the syndiotactic triads along with a drop in the isotactic triads; a cer-

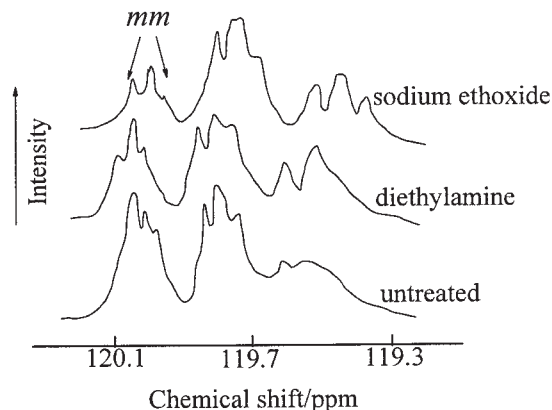


Figure 4 Expansion of ^{13}C NMR spectra of MAP polymers.

tain proportion of isotactic sequences were converted into syndiotactic sequences. This shows that the strong alkali abstracted the methine proton from an isotactic triad, and the nitrile was rearranged into a syndiotactic configuration.

Table II shows the changes in the tacticity of the MAP and WSP polymers treated with alkalis. The weak alkali behaved in the same way as the strong ones, but the changes in the tacticity of the polymers were less prominent. The effects of the alkalis on the tacticity of the polymers followed the order of the alkali strength: sodium ethoxide > sodium hydroxide > diethylamine. The effects of the alkalis on the tacticity of the WSP copolymers were less obvious.

Effect of alkalis on the stabilization exotherm of polyacrylonitrile

It is reported in the literature^{20,21} that ammonium itaconate and acrylamine were used as comonomers in polymerization to moderate the stabilization exotherm of polyacrylonitrile. In this study, the effect of alkalis on the stabilization exotherm of polyacrylonitrile was also studied. DSC curves of MAP and WSP copolymers were obtained. For untreated MAP, there was

TABLE II
Effect of Alkalis on the Tacticity of Polyacrylonitrile

Sample	Triad tacticity		
	(mm)	(mr)	(rr)
Untreated MAP	0.613	0.285	0.102
MAP treated with sodium ethoxide	0.419	0.298	0.283
MAP treated with sodium hydroxide	0.483	0.294	0.223
MAP treated with diethylamine	0.578	0.291	0.131
Untreated WSP	0.291	0.502	0.207
WSP treated with sodium ethoxide	0.236	0.521	0.243
WSP treated with sodium hydroxide	0.258	0.518	0.224
WSP treated with diethylamine	0.273	0.526	0.201

TABLE III
DSC Curve Parameters of Polyacrylonitrile

Sample	T_i (°C)	T_f (°C)	ΔQ (mJ/mg)
Untreated MAP	261.7	304.6	564.3
MAP treated with sodium ethoxide	248.1	298.7	538.7
MAP treated with sodium hydroxide	238.2	294.5	526.5
MAP treated with diethylamine	217.3	288.8	504.3
Untreated WSP	243.6	298.1	482.8
WSP treated with sodium ethoxide	237.8	295.6	479.2
WSP treated with sodium hydroxide	231.2	294.1	468.9
WSP treated with diethylamine	235.3	292.6	471.2

only one exothermic peak, but for MAP treated with diethylamine, there were two separated peaks. Effects of alkalis on the stabilization exotherm of WSP copolymers were less obvious. DSC curve parameters are given in Table III. Diethylamine was more effective for moderating the stabilization exotherm of MAP polymers than sodium ethoxide and sodium hydroxide. MAP treated with diethylamine had a lower starting exothermal reaction temperature. The two separated peaks and lower start temperature made the exothermic reaction temperature of MAP wider, alleviated the exothermic reaction, and moderated the stabilization exotherm of polyacrylonitrile. Heating MAP polymers in an oxidizing atmosphere caused the formation of a cyclic structure consisting of naphthyridine rings and crosslinking.²² The ammonia or amine groups in diethylamine were believed to act as catalysts in the cyclization reaction.

CONCLUSIONS

Laboratory studies of interactions between highly isotactic acrylonitrile homopolymers and alkalis in the solvent DMSO have shown that the effects of alkali on MAP are greater than those on ordinary polymers. As soon as polyacrylonitrile was added to a DMSO-alkali mixture, coloration occurred simultaneously. A solution containing diethylamine did not become as dark as a solution containing sodium ethoxide and sodium hydroxide.

$[\eta]$ of polyacrylonitrile decreased quickly with the addition of sodium ethoxide and sodium hydroxide,

and the effect of sodium ethoxide was more prominent than that of sodium hydroxide. As the concentration of sodium ethoxide and sodium hydroxide went beyond 0.01 mol/L, $[\eta]$ showed a trend of increasing. Within the first half-hour, there was a great drop in $[\eta]$ of MAP containing sodium ethoxide and sodium hydroxide, and then $[\eta]$ appeared to increase. $[\eta]$ of MAP containing diethylamine increased continuously along with time. The effects of alkalis on the tacticity of the polymers followed the order of the alkali strength, and a certain proportion of isotactic sequences were converted into syndiotactic sequences. Diethylamine was more effective for moderating the stabilization exotherm of polyacrylonitrile than sodium ethoxide and sodium hydroxide.

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